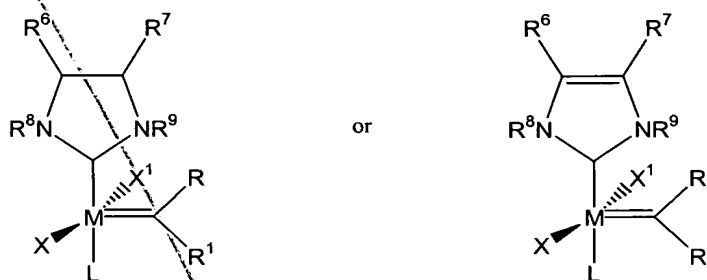


What is claimed is:

1. A method for preparing trisubstituted olefins comprising:
contacting a geminal disubstituted olefin with a terminal olefin in the presence of
a metal carbene metathesis catalyst.
2. The method of Claim 1 wherein the catalyst is of the formula:



wherein:

M is ruthenium or osmium;

X and X¹ are each independently an anionic ligand;

L is a neutral electron donor ligand; and,

R, R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

3. The method of Claim 2 wherein:

M is ruthenium;

L is selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, imine, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether; and,

X and X¹ are each independently hydrogen, halide, or a substituent selected from the group consisting of C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxy, C₃-C₂₀ alkylidenedione, arylidenedione, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl and halide.

4. The method of Claim 3 wherein:

M is ruthenium;

X and X¹ are each independently selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate;

L is a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl, C₁-C₁₀ alkyl, or cycloalkyl;

R is hydrogen; and,

R¹ is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

5. The method of Claim 4, wherein

X and X¹ are each chloride;

L is selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃; and,

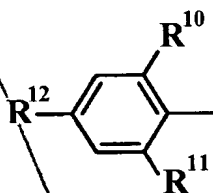
R¹ is phenyl or -C=C(CH₃)₂.

6. The method of Claim 5 wherein R⁶ and R⁷ together form a cycloalkyl or an aryl.

7. The method of Claim 5 wherein R^6 and R^7 are the same and are hydrogen or phenyl.

5 8. The method of Claim 5 wherein R^8 and R^9 are each independently a substituted or unsubstituted aryl.

9. The method of Claim 5 wherein R^8 and R^9 are each independently of the formula

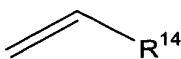


10 wherein

R^{10} , R^{11} , and R^{12} are each independently hydrogen, C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, aryl, or a functional group selected from hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

15 10. The method of Claim 9 wherein R^{10} , R^{11} , and R^{12} are each independently hydrogen, methyl or isopropyl.

11. The method of Claim 1 wherein the terminal olefin is of the formula:



20 wherein R^{14} is selected from the group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxycarbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl; and wherein R^{14} is substituted or
25 unsubstituted.

12. The method of Claim 11 wherein R^{14} is substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy and aryl, wherein the moiety is substituted or unsubstituted.
13. The method of Claim 12 wherein the moiety substitution is selected from the group consisting of halogen, a C_1 - C_5 alkyl, C_1 - C_5 alkoxy, and phenyl.
14. The method of Claim 11 wherein R^{14} contains one or more functional groups, wherein the functional group is selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.
15. The method of Claim 11 wherein R^{14} is a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen, wherein the functional group is substituted or unsubstituted.
16. The method of Claim 1 wherein the geminal disubstituted olefin is of the formula
-
- wherein R^{13} is selected from the group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxycarbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl; and wherein R^{13} is substituted or unsubstituted.
17. The method of Claim 11 wherein R^{13} is substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy and aryl, wherein the moiety is substituted or unsubstituted.

18. The method of Claim 12 wherein the moiety substitution is selected from the group consisting of halogen, a C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl.
- 5 19. The method of Claim 11 wherein R¹³ contains one or more functional groups, wherein the functional group is selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.
- 10 20. The method of Claim 11 wherein R¹³ is a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen, wherein the functional group is substituted or unsubstituted.
- 15 21. The method of Claim 1 wherein the disubstituted olefin is a substituted or unsubstituted α -functionalized olefin.
- 20 22. The method of Claim 21 wherein the α -functionalized olefin is a substituted or unsubstituted acrylamide.
- 25 23. The method of Claim 21 wherein the α -functionalized olefin is selected from the group consisting of a substituted or unsubstituted acrylate, vinyl ketone, and vinyl aldehyde.
- 30 24. The method of Claim 1 wherein the terminal olefin is gem substituted.
25. The method of Claim 1 wherein the trisubstituted olefin is prepared at room temperature.
26. A method for preparing di- or tri-substituted olefins comprising contacting a first substituted or unsubstituted electron deficient olefin with a second substituted or

unsubstituted electron deficient olefin in the presence of a metal carbene metathesis catalyst, wherein the first and second olefins are the same or different.

27. The method of Claim 26 wherein the first olefin is a substituted or unsubstituted styrene and wherein the second olefin contains an α -carbonyl group.

28. The method of Claim 27 wherein the second olefin is acrylate or acrylamide, and wherein the second olefin is substituted or unsubstituted.

29. The method of Claim 26 wherein the first and second olefins each contain an α -carbonyl group.

30. The method of Claim 26 wherein the first olefin is a substituted styrene and wherein the substitution occurs on one or more aromatic carbons.

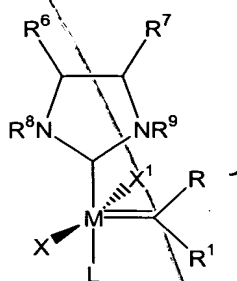
31. The method of Claim 26 wherein the first olefin is a substituted styrene and wherein the substitution occurs on the olefinic carbons.

32. The method of Claim 26 wherein the first olefin is an ortho-substituted styrene.

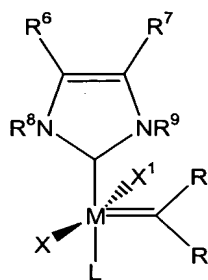
33. The method of Claim 26 wherein the first olefin is a terminal olefin and wherein the second olefin is an α -functionalized olefin.

34. A method for preparing di- or tri- substituted olefins comprising contacting a substituted or unsubstituted aliphatic olefin with a substituted or unsubstituted electron-deficient olefin in the presence of a metal carbene metathesis catalyst.

35. The method of Claim 34 wherein the metathesis catalyst is of the formula



or



wherein:

M is ruthenium;

X and X¹ are each independently selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate;

L is a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl, C₁-C₁₀ alkyl, or cycloalkyl;

R is hydrogen; and,

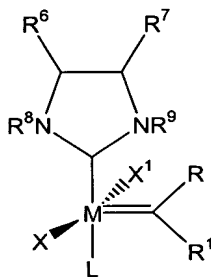
R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

36. The method of Claim 34 wherein the aliphatic olefin is a mono-, di- or trisubstituted olefin.

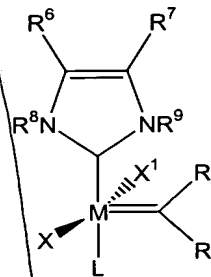
37. The method of Claim 34 wherein the aliphatic olefin is substituted one or more groups selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀

alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, wherein the substituent group is substituted or unsubstituted.

38. The method of Claim 37 wherein the substituent group is substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl, wherein the moiety is substituted or unsubstituted.
39. The method of Claim 38, wherein the moiety is substituted with one or more groups selected from a halogen, a C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl.
40. The method of Claim 34 wherein the aliphatic olefin includes one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.
41. The method of Claim 34 wherein the aliphatic olefin is 1-hexene and the electron-deficient olefin is methyl acrylate.
42. A method for preparing trisubstituted olefins comprising contacting a first substituted or unsubstituted styrene with a second substituted or unsubstituted α -functionalized olefin in the presence of a metathesis catalyst to form a cross-product and stilbene, and contacting the stilbene with unsubstituted α -functionalized olefin in the presence of a metathesis catalyst, wherein the catalyst is of the formula:



or



wherein:

M is ruthenium;

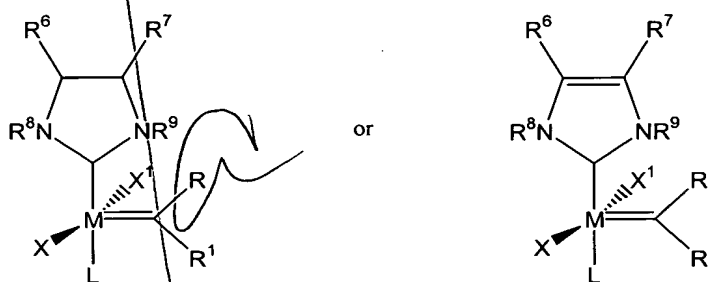
X and X¹ are each independently selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate;

L is a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl, C₁-C₁₀ alkyl, or cycloalkyl;

R is hydrogen; and,

R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

43. A method for the ring closing metathesis of an enone comprising contacting the enone with a catalyst of the formula:



wherein:

M is ruthenium or osmium;

X and X¹ are each independently an anionic ligand;

L is a neutral electron donor ligand; and,
R, R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

44. The method of Claim 43 wherein:

M is ruthenium;

L is selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, imine, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether; and,

X and X¹ are each independently hydrogen, halide, or a substituent selected from the group consisting of C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxy, C₃-C₂₀ alkyldiketonate, aryldiketonate, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl and halide.

45. The method of Claim 43 wherein:

M is ruthenium;

X and X¹ are each independently selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate;

L is a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl, C₁-C₁₀ alkyl, or cycloalkyl;

R is hydrogen; and,

R¹ is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional

group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

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